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THE FORMATION OF THE PHOTOGRAPHIC LATENT IMAGE

by DR. WILLIAM WEST

THE MAKING OF A PHOTOGRAPH involves a lengthy series of operations, from the manufacture of the sensitive film, through exposure, development, fixing, and often the conversion of a negative to a positive. All of these operations are necessary, but the heart of the matter is the exposure, for it is through variations in the intensity of light falling on the film in the camera, corresponding to variations in brightness and color of the scene, that the picture is made. The history of the photographic film during the hundredth of a second or so of a normal photographic exposure may be of some interest to those concerned in any way with the uses of photography. As for most scientific problems which we attempt to explain in detail, there is no finality to the answers, and certain aspects of the mechanism of the photographic process are at present subjects of lively controversy. Nevertheless, some of the main features of our modern concepts of the photographic process are probably almost as certain as scientific hypotheses ever are, and the following sketch of the concepts and the facts on which they are based may be of some interest to those concerned in a general way with photography.

A photographic film just after an exposure shows no change whatever visible to the eye, or, for that matter, to the most powerful visual or electron microscope. Nevertheless, an important change has occurred, when the film is placed in a developer, those parts which were exposed to light are changed chemically to a deposit of dark, finely divided metallic silver, while the unexposed parts are unaltered, with the familiar result of the production of a negative image of the scene to which the film was exposed. In some way or other, the image, which we finally realize on development, was hidden or latent in the exposed but undeveloped film, and we say that the exposed film contains a latent image. The important property of the latent image is that it can greatly accelerate, or catalyze, the production of silver when the film is immersed in a developer.

We can obtain some idea of what the latent image might be by working back from the chemistry of the development process. The sensitive material in a photographic film is a salt of silver, usually silver bromide containing a little iodide, suspended as minute, but often well-formed, crystals in a layer of gelatin. The illustration to the left shows a photomicrograph of such a suspension, or emulsion, as it is

technically called, in a highly dilute form – the triangular and hexagonal bodies are the crystals of silver halide, about one thousandth of a millimeter in diameter in a highly sensitive emulsion. Such photomicrographs can be made in red light, to which the emulsion is relatively insensitive, see also cover illustration.

Above are shown the grains of an exposed emulsion at two stages of development, as revealed by the electron microscope. After exposure, the grains were dissolved away by hypo, leaving the metallic silver formed by development. The black filaments in the figures constitute the developed silver, which appear against the ghost of the original grain in the position which they occupied before the silver halide was dissolved. On the left, development has just started. Isolated dark clumps of

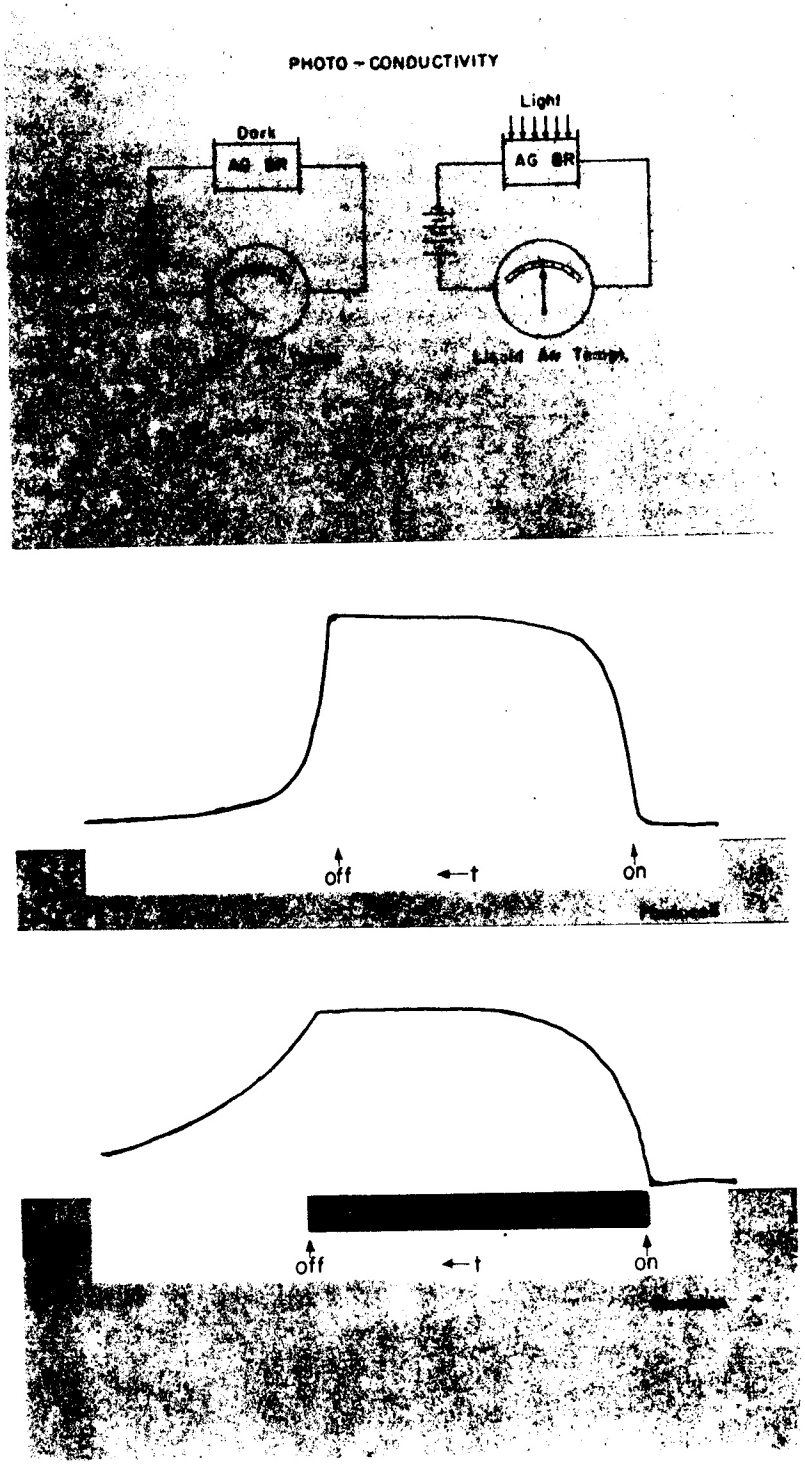
filamentary silver appear, mostly at the edges of the grains. As development proceeds, the clumps extend, until finally, as shown above, the whole grain has been converted to metallic silver. The essential chemistry of development is simple. The original grains of silver bromoiodide are composed of positively charged silver ions and negatively charged halide ions, while the developer is a reducing agent, that is, a compound which readily transfers electrons to other molecules. Electrons from molecules of developer combine with silver ions of the grain to form uncharged atoms of metallic silver, which aggregate to form the visible masses of silver constituting the photographic image. This reduction to silver occurs only in grains which contain latent image as the result of exposure, and the discrete spots at which

development may be seen to commence are probably the sites of latent image centers. Now it is known that minute particles of metal often catalyze or hasten the reduction of the corresponding metallic ions, or even of the ions of a different metal, and it is reasonable to suppose that the latent image center which catalyzes the development process is a minute particle of metallic silver. There are also good reasons for supposing that the latent image center contains a small number of silver atoms, more than two, but probably a minimum of three or four, although some centers seem likely to contain a score or two of silver atoms. All that is required to render a grain developable is that a single latent image center be formed by exposure. An average grain of a highly sensitive emulsion contains about a billion silver ions, and if all these are reduced to metallic silver by a single latent image center containing say 10 silver atoms, we see that about 100 million times as much silver is formed by development as is formed directly by light. It is this enormous multiplication of the effect of light by the development process that renders the photographic emulsion so extremely sensitive to light.

The effect of exposing a photographic film is therefore to produce one or more latent image centers in the grains of silver halide which have received light, and these latent image centers are minute particles containing a few atoms of silver. Our problem now is to find out how this happens.

Although no visible change occurs in the grains of an emulsion during exposure, it is possible by electrical means to show that something is going on during the absorption of light. If a crystal of silver bromide at low temperature is made part of an electrical circuit containing a battery and a very sensitive meter, as above, right, no electric current will be observed in the dark, but immediately light is turned on the crystal, a flow of current takes place, the current increasing proportionally with the intensity of the light. The crystal is said to become photoconductive. The nature of the currents shows that the carriers of electricity are electrons and not silver ions or bromide ions, and we conclude that the first effect of absorption of light by a crystal of silver halide is to cause a flow of electrons within the crystal. Photoconductivity can be observed in ordinary photographic emulsions; the illustration to the right shows the record of such a photocurrent. The white line is the trace of the pointer of the meter in a very sensitive d.c. amplifier, and at the right of the figure, which indicates a situation when the film is not illuminated, the position of the meter indicates that no photocurrent is flowing. Immediately the shutter is opened, a flow of current begins, rapidly attains a steady value, and begins to drop immediately when the shutter is closed. For comparison, the record of an ordinary vacuum photoelectric cell obtained by the same amplifier and meter is illustrated. Although the rise and fall of the photocurrent in the emulsion is somewhat slower than that for the photocell, the electrical response of the emulsion on illumination is on the whole quite similar to that of the photoelectric cell.

Photoelectric conductivity is not the only type of electrical conductivity shown by silver halide crystals. The silver bromide crystal is composed of silver ions and bromide ions, and a few of these charged particles can move in an electrical field, yielding an electrolytic current of exactly the same general nature as that involved in the electrolysis of salt solutions. In fact, it is possible to plate out metallic silver at the cathode in the electrolysis of solid silver bromide just as one plates silver from a silver plating solution. The electrolytic current in silver halides can be easily



distinguished from the photocurrent by the facts that it is not changed by exposure, that it rapidly decreases on lowering the temperature, and that the carriers of electricity are much less mobile than those involved in the photocurrents. It is known that only silver ions move in solid silver halides and of these, at room temperature, only a very small proportion. The illustration to the right shows how any motion of ions in the solid crystalline lattice of silver halides can occur at all. The crystal is made up of a regular array of the silver ions, shown shaded, and of larger bromide ions, shown as the larger circles. Where the lattice is perfect, the close packing of the ions prevents any from jostling their way out, and all that happens is that the ions vibrate about fixed positions of equilibrium. Occasionally, however, a silver ion acquires an abnormally large amount of energy and jumps from its regular position to a so-called interstitial position, as shown in the diagram. The vacancy in the regular lattice can now be filled by an adjacent silver ion, but the vacancy reappears at the site from which the silver ion has jumped: this is equivalent to the motion of charge and can produce a current. Similarly, the interstitial ions can displace a regular ion from its site which is equivalent to the motion of interstitial silver ions.

We have now seen two important electrical phenomena which might be concerned with the photographic process; at room temperature and at temperatures not too far below room temperature, a few silver ions move about the crystal whether in the light or in the dark, and during exposure to light, electrons move about the crystal in amounts proportional to the intensity of the light. In some way or other, it seems likely that these phenomena must be connected with the formation of the latent image.

At this stage in our investigation, it may help to consider the chemistry of the over-all reactions associated with the formation of latent image. The known chemical changes which occur as a result of exposure can be explained by supposing that a bromide ion in the lattice loses an electron on absorbing light, according to the scheme:

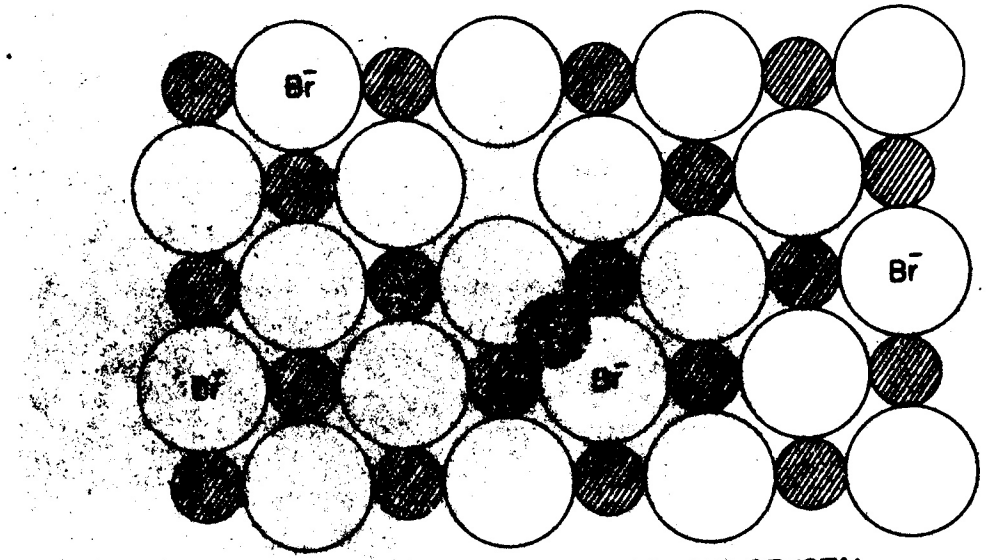
$$\mathrm{Br^-} + \text{light} = \mathrm{Br} + \text{electron},$$

and that this electron is captured by a silver ion, forming a neutral silver atom,

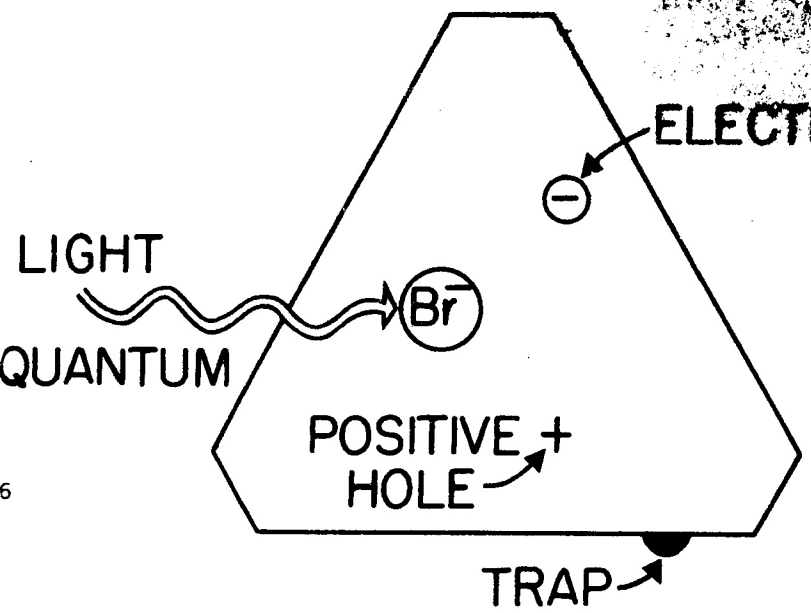
$$\mathrm{Ag^+} + \text{electron} = \mathrm{Ag}.$$

We have already argued that the latent image is composed of a few silver atoms. The bromine atoms left as a result of the loss of electrons by bromide ions could escape from the crystal as molecular bromine, and in fact, bromine is known to be evolved during prolonged exposures of silver bromide and we have indirect evidence of its occurrence in the shorter exposures involved in latent image formation. But at the same time, the existence of photoconductivity during photographic exposures shows that the bromide ion cannot lose its electron to an adjacent silver ion, since the passage of the electron over such a small distance would not produce a measurable current. The electron liberated by the light must become free to wander over considerable volumes of crystal before it is finally captured by a silver ion, and the whole operation of forming the silver atom and liberating the bromine must be a good deal more complicated than these simple chemical equations suggest.

The diagram, on page 66, illustrates what actually seems to happen. Here, a bromide ion in a grain of silver bromide has absorbed a light quantum, and an elec-



A (100) PLANE IN A SILVER BROMIDE CRYSTAL, ILLUSTRATING FRENKEL DEFECT

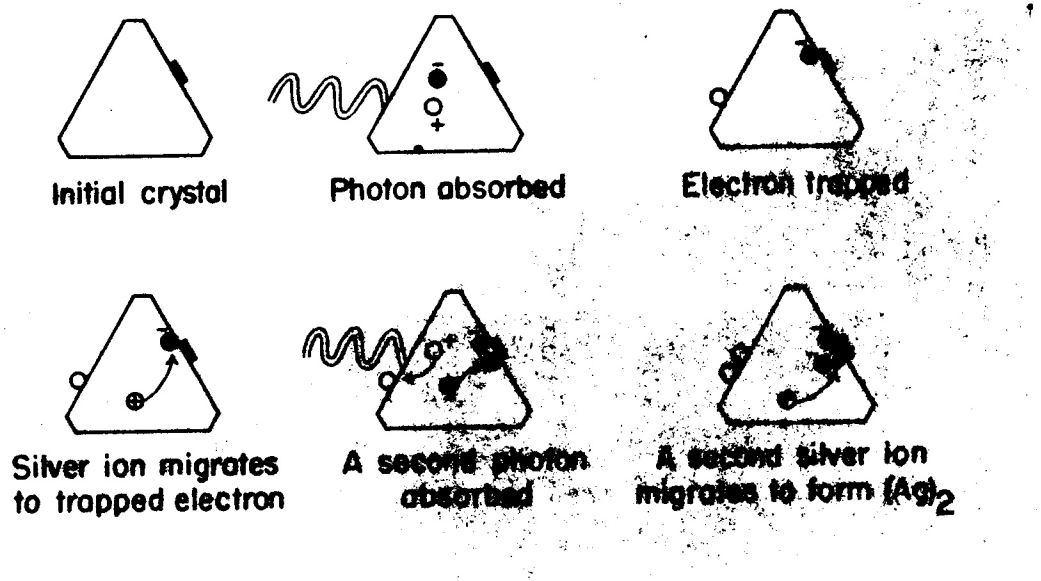


tron has been driven out of the ion and is moving rapidly about the crystal. Now, chemically, a bromide ion which has lost an electron is a bromine atom, but this bromine atom in the crystal has special properties arising from the mere fact that it is contained in a crystal otherwise composed of positive and negative ions. Since an electron carries a negative charge, the region in the crystal which lost the electron is deficient in negative electricity, that is, it carries a positive charge. Our bromine atom in the crystal is therefore in a region of positive charge, and to emphasize this aspect of its behavior, we call it a positive hole. This region of positive charge does not stay fixed in the crystal, for the hole can be filled by an electron from an adjacent bromide ion, which, in turn, becomes the seat of the positive charge, and in this way the positive hole moves about the crystal like a positively charged electron. As the result of absorption of light, we have, therefore, running about in the crystal, a negatively charged electron and a positively charged hole, and since unlike charges attract, there is a possibility that the two will meet and recombine. If they do so, a bromide ion is regenerated, and no over-all chemical change has occurred in the crystal. Suppose, however, there is a spot in the crystal which can attract and hold one of the charges before it has met the other. If, for example, the hole is held or trapped at this spot, it can no longer overtake and combine with the electron, leaving the electron free to combine with a silver ion to form a silver atom and so initiate the formation of a latent image center.

Now, it is found that the purer one makes silver halides, the less sensitive they become photographically. Photographic sensitivity belongs to the interesting group of phenomena, of great importance in the whole chemistry and physics of solids, in which behavior is profoundly modified by the merest traces of foreign material, impurity as the chemist would customarily designate them. Transistor action depends on minute traces of elements such as arsenic or boron in germanium, often to the extent of much less than one part per million; the luminescent powders of television picture tubes and in fluorescent lamps owe their properties to traces of certain foreign metal ions in a matrix of zinc sulfide or similar compound, and the photographic emulsion owes its great sensitivity to light to trace amounts of the proper foreign material.

In very pure silver bromide, it seems that the photoelectrons and positive holes simply recombine, and the absorbed light produces no chemical change. In order to achieve high photographic sensitivity, it is necessary to keep the electron and the positive hole apart, and the fundamental effect of those impurities which confer high photographic sensitivity is to act in this way. The impurities act, so to speak, as traps for the electrons and holes, immobilizing them, preventing their coming into contact and recombining.

Long before the modern picture of photographic sensitivity had been evolved, practical emulsion makers had realized that not only was gelatin a convenient medium in which to suspend the emulsion grains, but that it greatly influenced the sensitivity of the film. In the late '20's, a classic series of studies by Sheppard at the Eastman Kodak Laboratories showed that gelatin owed its sensitizing effects to small amounts of sulfur compounds, which, under the conditions of emulsion making, could react with silver halide and form traces of silver sulfide at the surface of the grains. The silver sulfide in fact acts as a sensitizing impurity


Initial crystal
Photon absorbed
Electron trapped
Silver ion migrates to trapped electron
A second photon absorbed
A second silver ion migrates to form $(Ag)_2$

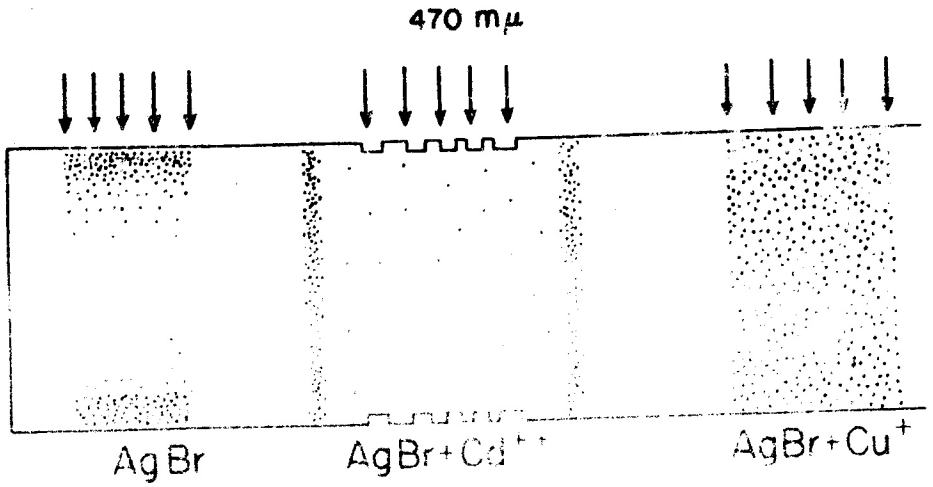
trapping either the electrons or the positive holes, and preventing recombination. Sheppard himself thought that silver sulfide trapped electrons. The first detailed account of latent image formation, by Gurney and Mott, is illustrated on the left. We have first an unexposed grain, which contains a trace of silver sulfide; then, the grain has absorbed a quantum of light, and a free electron and a positive hole have been formed. The electron roams through the grain at a speed of about 5 miles per second at room temperature, and is quickly trapped by the minute speck of silver sulfide at the surface. The positive hole also reaches the surface, where it becomes an adsorbed bromine atom. The trapped electron makes the sensitivity speck negatively charged and can attract an interstitial silver ion, which, as we saw, were mobile at room temperature. The mobile silver ion wanders up to the trapped electron and combines with it to form a silver atom. If, now, a second quantum is absorbed by the grain, a second photoelectron can be trapped by the silver atom already formed and the corresponding positive hole, after liberation at the surface as a bromine atom, can combine with the first bromine atom and leave the grain as a bromine molecule. Another silver ion wanders up to the trapped electron, combines with it, and we now have a silver center consisting of two atoms. This sub-latent image does not itself render the grain developable, but repetition of the process once or twice again will give us a stable latent image which will permit the grain to be developed even if the development process is delayed for months after the exposure.

This view of the photographic process explains a number of observed facts and suggested new results, especially on effects at low temperature, which were experimentally verified. Recently, however, various workers have suggested that silver sulfide acts rather as a trap for positive holes than for electrons, J. W. Mitchell of the University of Bristol being a particularly active advocate of the revised version of the original hypothesis. In the modified scheme, an electron is captured directly by a silver ion in a specially active site of the surface to form a silver atom, which is not very stable and will surely react with bromine or a positive hole unless the hole is very deeply trapped. The silver sulfide molecule at the surface of the photographic grain is supposed to trap the hole, and if, while the hole is trapped, a second electron and silver ion combine at the site of the first silver atom, a more stable diatomic silver molecule is formed. Repetition of the process finally leads to the appearance of a stable latent image center. Argument on points of detail like this might appear to some similar to the debates of the medieval schoolmen on the number of angels that can stand on the point of a needle, but of course the difference is that we can obtain objective answers to matters of scientific detail. These details are important, not only in satisfying one's intellectual curiosity and sense of understanding, but also in technological practice. In the present case, for example, the lines of thinking of practical emulsion makers may be definitely influenced by what they think the function of silver sulfide in the emulsion may be.

As a final example of research on fundamental photographic processes, I should like to refer briefly to some recent experiments which use not normal photographic grains, but thin crystals of silver bromide made by melting the material and squeezing it into sheets of single crystals between glass plates. We can then separate the sheets from the glass plates and carry out experiments in which this

readily manipulable, relatively large single crystal acts to some degree as a model of the individual photographic grain. When such sheets are exposed to light and developed, very regularly shaped silver bodies are formed, each one of which originates in a single latent image center. The illustration directly below shows a photomicrograph of a portion of such a sheet after exposure and development. Only the lower part of the sheet was exposed; on the right for a short time, on the left for a longer time. You will see that the short exposure produces few latent image centers and few developed silver bodies, while the longer exposure produces more.

The results on the diagram to the right illustrate the great effects which can be brought about in these sheet crystals by introducing traps for positive holes. Here we are dealing not with the microscopically invisible particles of latent image, but with the visible images of print-out silver which, as is commonly known, can be formed without development in silver halide, including ordinary emulsions, by prolonged exposure. On the left is a diagramatic section of a crystal of pure silver bromide which is exposed on its upper surface to a beam of light of such a wavelength that it can penetrate the whole crystal and at the same time be absorbed



Distribution of photolytic products in thin AgBr crystals

enough to bring about photographic effects. In spite of the fact that the whole crystal is bathed in photo-active light, the print-out silver is formed only near the surface of incidence and exit of the light, with practically none in the interior. The reason for this distribution of the photo-product seems to be that in the middle of the crystal the positive holes produced during exposure cannot diffuse away quickly to the surface, and therefore combine with electrons and silver atoms, while nearer the surface, by diffusion to the exterior of the crystal, they are prevented from combining with the silver. The material on the right contains a small amount of cuprous salt in the matrix of silver bromide. The cuprous ion, which bears a single positive charge, rather readily can transfer an electron to a positive hole; the original hole becomes an innocuous bromide ion, while the former cuprous ion, after losing an electron, becomes a doubly positively charged cupric ion. The positive charge formerly on the hole is now carried by the cupric ion, but whereas the hole was mobile and could chase electrons all over the crystal and recombine with them, the cupric ion is rigidly fixed in the crystal and the chance of combining with an electron is greatly reduced. As a result of this capture of positive holes, about 10 times or more print-out silver is formed by the same absorption of light in the crystal containing the copper impurity than in a pure crystal, and moreover, the silver is formed throughout the whole thickness of the crystal.

This discussion of the scientific study of the latent image emphasizes those interesting effects of trace amounts of material in a mother matrix which are being recognized as of prime importance in many branches of chemistry and physics. Another point is that we must understand the action of what often seems at first sight the mysterious effects of these traces if we are to control them. When the English amateur photographer who first succeeded in making a usable emulsion in gelatin conceived the idea, he was merely interested in a convenient method of making a uniform coating of the sensitive material on glass. When, shortly afterwards, a greatly increased sensitivity of the gelatin emulsions over the old inconvenient wet collodion emulsions was observed, especially after heating, this was an unexpected bonus. These early workers had, of course, no idea that they were increasing sensitivity by trapping positive holes or electrons by trace amounts of silver sulfide formed by reaction of small amounts of sulfur compounds in the gelatin with silver bromide – the very concept of the electron had not yet arrived. The photographic industry got off to a fair start by means of unceasing empirical experimentation, intuition and rule of thumb, but there was constant trouble for the emulsion maker when, for example, he changed from a batch of gelatin to which he had become accustomed to a new batch derived from cows which had grazed on a pasture less luxurious in sulfur-bearing plants than those from which his old material had been derived. Only by the preparation of material of the greatest possible purity and then observing the effects of controlled additions of known addenda can we achieve the necessary understanding of these strange effects in solid-state chemistry and physics. Active work of this nature is being carried out in university laboratories and in the laboratories of several types of industry, including the communications, electronic, electrical, metallurgical, and photographic industries, and we can be certain that with increased understanding of these effects, there will emerge many new products and new devices.

CHARLES CLIFFORD

by HELMUT GERNSHEIM

AT THE TIME OF OUR EXHIBITION "A Century of Photography from the Gernsheim Collection" in the Art Museum at Gothenburg in spring 1956, the Director, Dr. Westholm, asked me to look through several boxes of miscellaneous photographs in the Museum's possession. The most exciting were fifty-three 12" x 16" prints of Spanish subjects, which I was able to identify as the work of Charles Clifford, an Englishman who lived in Madrid and was Court photographer to Queen Isabella II. They date from the late 1850s and fall roughly into three groups: 8 landscapes; 29 architectural subjects in Toledo, Avila, Malaga, Granada, Saragossa, Seville, Madrid, Burgos, Cadiz, Segovia and Barcelona; 16 photographs of art objects in the so-called Treasure of the Dauphin, inherited by Philip V from his father the Dauphin (son of Louis XIV). I understand from Dr. Westholm that this treasure is now exhibited in the Prado Museum, but in Clifford's time it was housed in the Royal Armoury *(Armeria Real)* in a wing of the Royal Palace, Madrid.

My interest in this photographic treasure-trove was naturally great, for photographs by Clifford are rarely met with outside Spain, and with the exception of one view of Burgos Cathedral which is also in the Gernsheim Collection, all the subjects at Gothenburg were new to me. In fact, his photographs at Gothenburg form the largest collection known to me. I gladly respond to the suggestion from the George Eastman House to communicate the little I have been able to find out about the man and his work.

Though an architectural photographer of unusual merit, comparable with MacPherson, Bisson and Baldus, details of Clifford's life and career are as elusive as examples of his work. Spain, unlike Italy, was not a country much frequented by tourists in the nineteenth century. It was not on the usual itinerary of the Grand Tour, and hence few of Clifford's photographs found their way into English print collections. Since Clifford seldom sent his pictures to photographic exhibitions, although he was a member both of the Société Française de Photo-

PANEL 12

EXPOSING AND PROCESSING FILM

SCHEMATIC DIAGRAMS

(Light-sensitive layer only)

△ Unexposed silver halide crystal

△ Exposed silver halide crystal

▲ Black metallic silver grain

△ Dissolved silver halide crystal and reaction byproducts

FILM: Before Exposure

ORIGINAL SCENE

Light Reflected From Scene

FILM: After Exposure (Latent Image)

After Development (Silver Image)

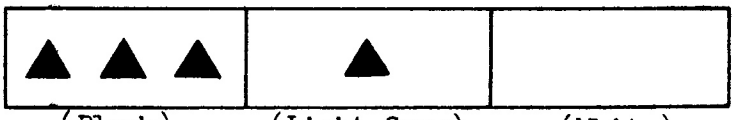
After Stop Bath

After Fixing Bath

After Washing

After Drying

THE NEGATIVE



EXPOSING AND PROCESSING PAPER

△ Unexposed silver halide crystal

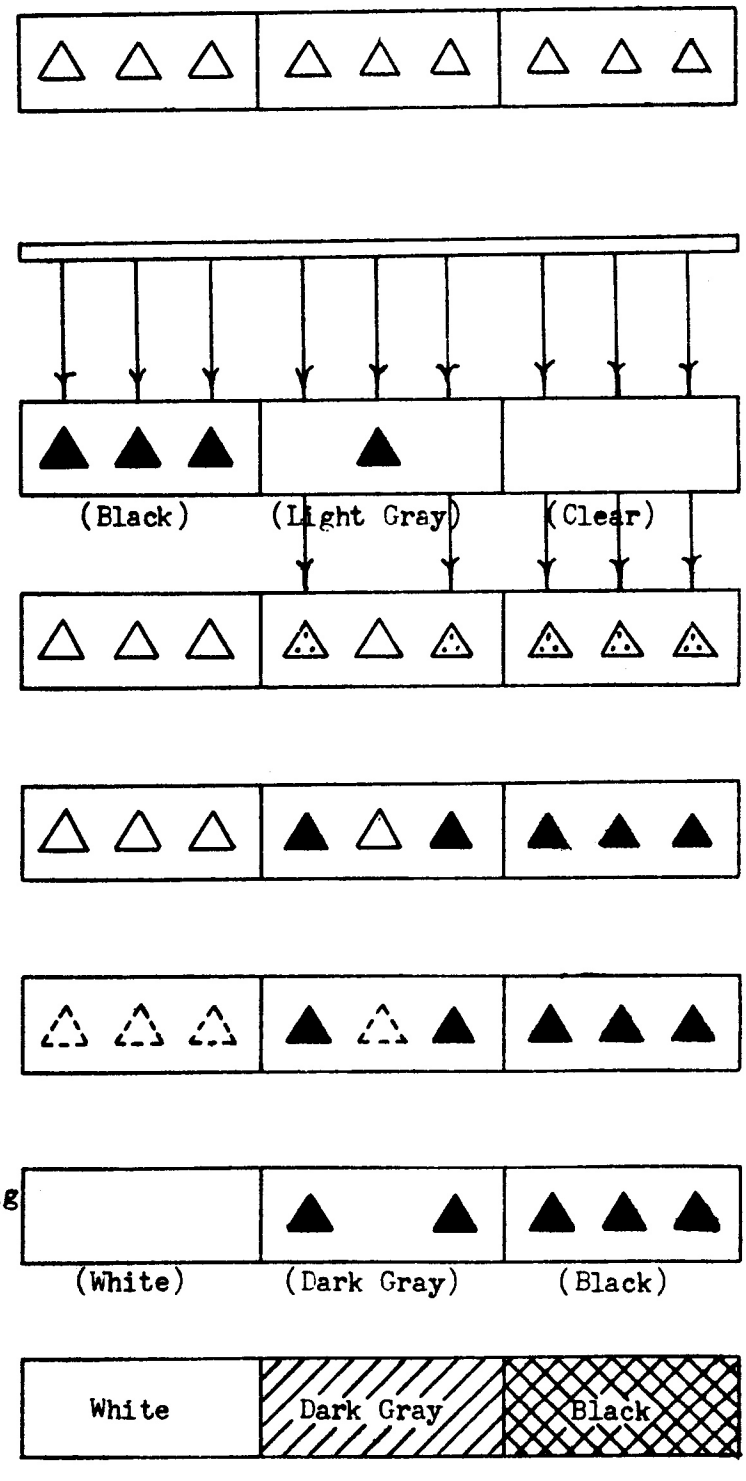
△ Exposed silver halide crystal

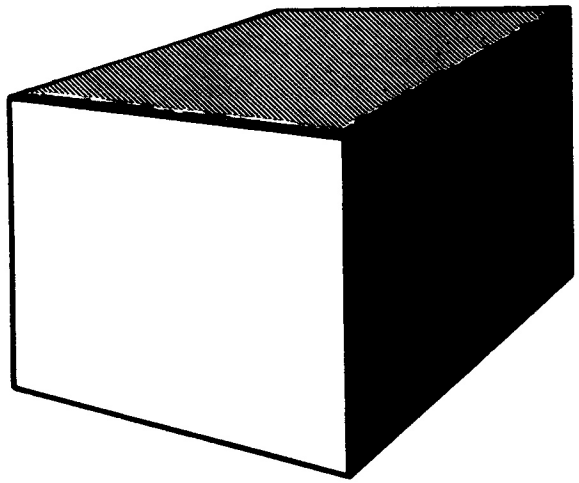
▲ Black metallic silver grain

△ Dissolved silver halide crystal and reaction byproducts

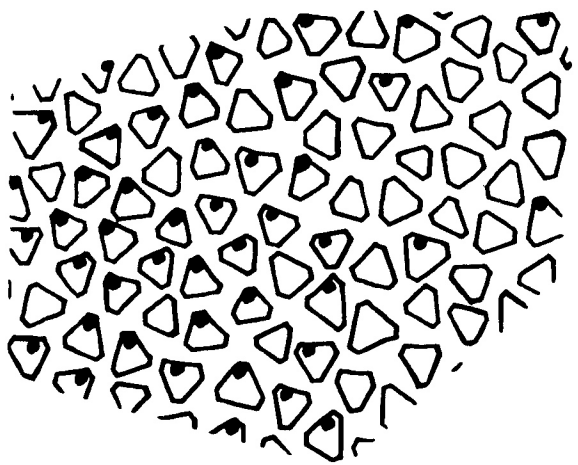
SCHEMATIC DIAGRAMS

(Light-sensitive layer only)

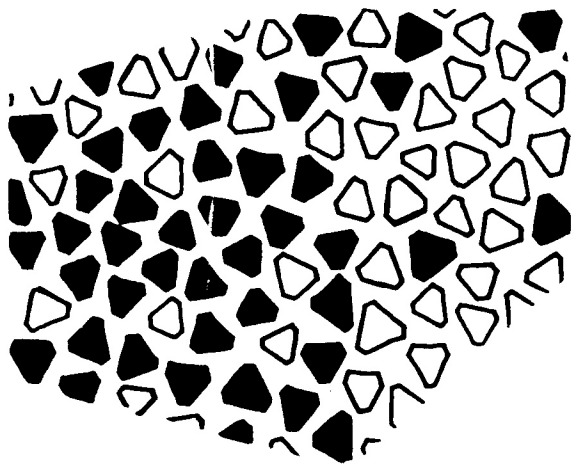




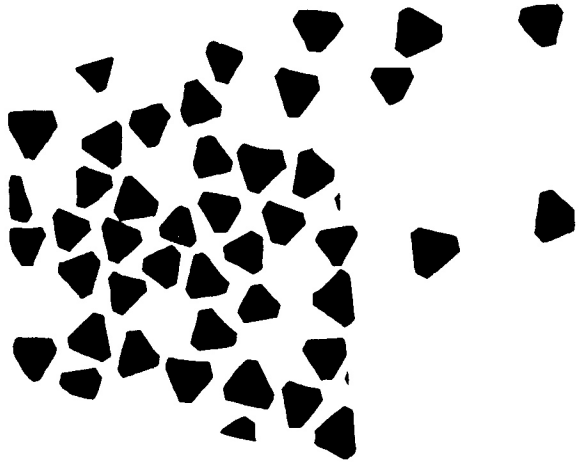
← SUBJECT



EXPOSURE



DEVELOPMENT



FIX-WASH